

AD-A239 146



REPORT DOCUMENTATION PAGE

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2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		1b. RESTRICTIVE MARKINGS	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 1991-15		3. DISTRIBUTION/AVAILABILITY OF REPORT Distribution Unlimited	
6a. NAME OF PERFORMING ORGANIZATION University of Pennsylvania	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION ONR	
6c. ADDRESS (City, State, and ZIP Code) University of Pennsylvania Department of Chemistry Philadelphia, PA 19104-6323		7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION DARPA	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 3701 N. Fairfax Drive Arlington, VA 22203-1714		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) "XPS STUDY OF SULFONATED POLYANILINE"			
12. PERSONAL AUTHOR(S) J. Yue, J. Epstein and A.G. MacDiarmid			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 1-1-91 TO 10-31-91	14. DATE OF REPORT (Year, Month, Day) August 7, 1991	15. PAGE COUNT 2
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>The first XPS experimental study of core level spectra of self-doped conducting polyaniline has been presented. Through use of the XPS technique, differing influences of SO₃ and Cl⁻ on the N 1s core level have been demonstrated.</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Alan G. MacDiarmid		22b. TELEPHONE (Include Area Code) 215-898-8307	22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

GRANT NO.: N00014-90-J-1559

R & T CODE NO.: A400004DF3

TECHNICAL REPORT NO.: 1991-15

"XPS STUDY OF SULFONATED POLYANILINE"

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Published in
PMSE Preprints, (In Press 1991)

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Department of Chemistry
Philadelphia, PA 19104-6323

August 7, 1991

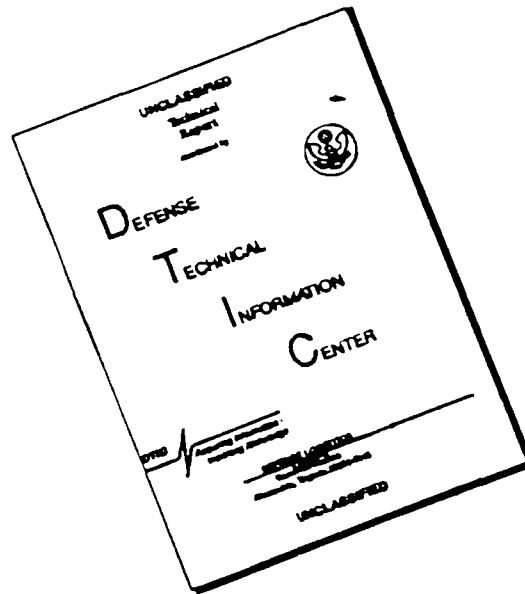
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XPS STUDY OF SULFONATED POLYANILINE

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INTRODUCTION

The polyaniline family of polymer has been under intense study because of its facile chemistry, and ability to be both protonical and oxidatively or reductively doped to a highly conducting state [1, 2]. The ideal emeraldine base (EB) oxidation state of polyaniline contains equal number of alternating amine and imine repeat units, Fig. 1(a), [2]. When EB is doped by a protonic acid, the protonation occurs preferentially on the imine nitrogen sites [2], as for example shown for the emeraldine hydrochloride salt (ES-HCl) in Fig. 1(b). Recently, the sulfonated polyaniline (SPAN), the first self protonic acid doped polyaniline, Fig. 1(c), was reported [3]. Transport studies on this self doped polymer show that there is a greater charge localization present in SPAN than in ES-HCl [4]. In order to gain insight into the difference in structural and electronic properties among doped, undoped, externally and internally doped emeraldine, a study using X-ray photoelectron spectroscopy (XPS) was undertaken.

The results, reported here, demonstrate that the stoichiometry of SPAN indeed is 0.5 $-SO_3^-$ group per phenyl-nitrogen unit, that the doping level is stable under vacuum (in contrast to reduced surface doping level for ES-HCl) and that there is greater charge localization in SPAN as compared with ES-HCl. The origins of these differences are discussed.

EXPERIMENTAL TECHNIQUES

Emeraldine base, emeraldine hydrochloride powder [5] and sulfonated polyaniline (SPAN) [3] were synthesized by using previously described methods. The vacuum dried sample powders were mounted onto a standard sample holder by using a double-sided adhesive tape. Core level spectra were obtained utilizing a Perkin-Elmer Physical Electronics Model 550 ESCA system with a Mg K α X-ray source (1253.6 eV). The X-ray power supply was run at 12 KW and 10 mA. The pressure in the analysis chamber during scans was kept below 10^{-8} torr. The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors. N 1s spectra, after background subtractions, were decomposed into suitable components consisting of a Gaussian line shape with a Lorentzian broadening function. All fitting parameters, including the number of components, widths and intensities were freely adjustable and determined for each spectrum with an iterative, least-square fitting routine.

Occasionally, small differences were found in the binding energies determined for the same species in different samples. Thus during attempts overlaying binding energy spectra of supposedly identical samples, it was accordingly necessary to make a small energy adjustment to achieve good overlap. In every case, these adjustments produced complete overlay of all peaks, indicating that these shifts are due to sample-dependent charging effects, other possible chemical and physical causes can not be precluded.

The binding energy of C 1s was adjusted to 285.0 eV based on the studies of polyaniline [6, 7, 8] in order to compensate the charging effects for each sample; it was taken as the reference for the other core level peaks. C 1s spectra were smoothed by a three point averaging routine [7].

RESULTS AND DISCUSSION

N 1s of EB

Emeraldine base has a simple, symmetric N 1s line centered close

to 398.6 eV, shown in Fig. 2(a). This is expected from the idealized structure of the emeraldine base backbone. The peak centered at 398.9 eV is assigned to the amine nitrogen [9, 10]. The other located at 397.5 eV is attributed to imine nitrogen atoms [9]. The nearly 1 to 1 ratio of amine and imine nitrogen is consistent with the idealized EB structure [2].

N 1s of SPAN

Dramatical change in N 1s line shape can be observed when EB is sulfonated by fuming sulfuric acid, $H_2SO_4(SO_3)$, Fig. 2(b). As compared with N 1s line of EB, the imine nitrogen peak at 397.5 eV of EB disappears completely and the cationic radical nitrogen peak [9] appears at 400.7 eV. Hence these XPS spectra show that the imine nitrogen atoms are completely protonated by the intrinsic acid $-SO_3H$. The main N 1s peak of SPAN at 399.4 eV has a resolved shoulder on the high energy side at 400.7 eV. The shoulder is believed to arise from the localized polarons in SPAN. By comparing N 1s lines, polaron in SPAN is more localized than that of in EB doped by HCl (see content below). The localization perhaps is caused by a strong electrostatic interaction between the $-SO_3^-$ function groups and cationic radical nitrogen atoms. Furthermore larger torsional motion introduced by an interaction between $-SO_3^-$ and hydrogens on the adjacent phenyl ring can somewhat break the π electron conjugation and tend to localize the positive charges during and after self doping process. Therefore there is a formation of local distortions of the polymeric lattice around such localized charges in the doping process. In the light of above discussion an enhancement of asymmetry at higher binding energy side is not surprising. Despite the self protonation accesses at imine nitrogen, the original structure of amine nitrogen centered at 399.1 eV remains almost unchanged.

The ratio of amine nitrogen and cationic radical nitrogen atoms is 1:1 indicating that the doping level reaches its maximum, i.e. 50%, which is consistent with the structure proposed previously [3]. Rough 1:2 atomic ratio of sulfur and nitrogen from XPS data again supports that essentially half of phenyl rings are monosubstituted by sulfonic group [3] leading to a self doped state.

N 1s of emeraldine hydrochloride

Although the N 1s main peak of ES-HCl in Fig. 2(c) does not show clear splitting, the peak envelope obviously does not originate from a single component. Absence of shoulder at higher binding energy side indicates that there is no unique difference between amine and cationic radical nitrogen atoms in binding energies. As comparing with SPAN, the positive charge in ES-HCl is more delocalized. It appears that the N 1s core level line shape of ES can be decomposed into contributions from three inequivalent nitrogen species. The peak centered at 402.2 eV is attributed to most positively charged nitrogen sites perhaps in the vicinity of chloride ions and the peak located near 400.4 eV is attributed delocalized positively charged nitrogen atoms. It should be noted that the chloride ion with charge of $-e$ is located between polymer chains. It produces an electric field locally at or near half of the nitrogen sites, causes those nitrogen atoms to appear "more" positive than the others.

It is of interest to compare the integrated intensities of positively charged nitrogen atoms (with core level binding above 400.5 eV) to that of uncharged amine sites at 399.1 eV. The results show that the ratio of positively charge to neutral amine nitrogen atoms is 33:67. This 33% positive charged nitrogen is substantial lower than that of 50% obtained by chemical analyses in fully doped bulk ES-HCl [2, 5] and surface (XPS) analysis for SPAN. The ratio of counterions (Cl^-) to total nitrogen atoms in the polymer chains can be employed to determine the doping level of emeraldine system [5]. The argument of 33% doping level from analysis of N 1s XPS spectra can be supported by atomic ratio of chlorine and nitrogen, of $[Cl]/[N]=0.29$ obtained from integrating the Cl 2p and N 1s XPS spectra. The reduced surface doping level of ES-HCl at high vacuum likely arises from desorption of HCl or Cl_2 after the sample was pumped at room temperature. The substantially higher amine content (67%) is also consistent with the removal of Cl_2 . A comparison with a measured $\sim 50\%$ doping level for the SPAN system supports that the protonation level at high temperatures [11] or vacuum can be stabilized

via self protonation.

The proposed structure for nitrogens is also consistent with the full width at half maxima (FWHM) of the different components. The component at 402.1 eV, which is believed to be the most influenced by the presence of the chloride ions, has FWHM of 2.0 eV, while the FWHM of 400.2 eV which is less affected by chloride ion is 1.8 eV. The least influenced amine nitrogen atoms have 1.6 eV which is essentially same as that of EB. The more delocalized positive charge for ES-HCl as compared with SPAN is consistent with that it has higher conductivity [4].

CONCLUSION

The first XPS experimental study of core level spectra of self doped conducting polyaniline has been presented. Through use of the XPS technique, differing influences of $-\text{SO}_3^-$ and Cl^- on the N 1s core level have been demonstrated. For the self doped samples, the protonation is stabilized by the binding of the $-\text{SO}_3^-$ groups to the polymer backbone. In contrast, loss of some Cl^- or HCl at high vacuum condition causes deprotonation of ES-HCl. There is a greater charge localization in the SPAN system than that of ES-HCl attributed to the proximity of the $-\text{SO}_3^-$ groups on the polymer chain. The agreement between the results of the present investigation using XPS and results from other means strongly supports the structure proposed for self doped conducting SPAN.

ACKNOWLEDGEMENTS

This work is supported in part by DARPA through contract monitored by USONR.

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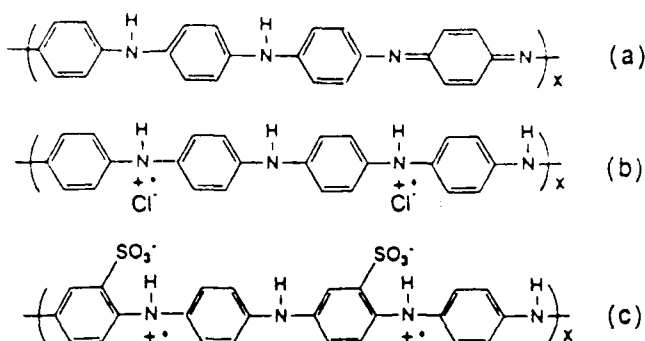


Fig. 1 Structures of (a) emeraldine base, (b) emeraldine hydrochloride and (c) sulfonated polyaniline.

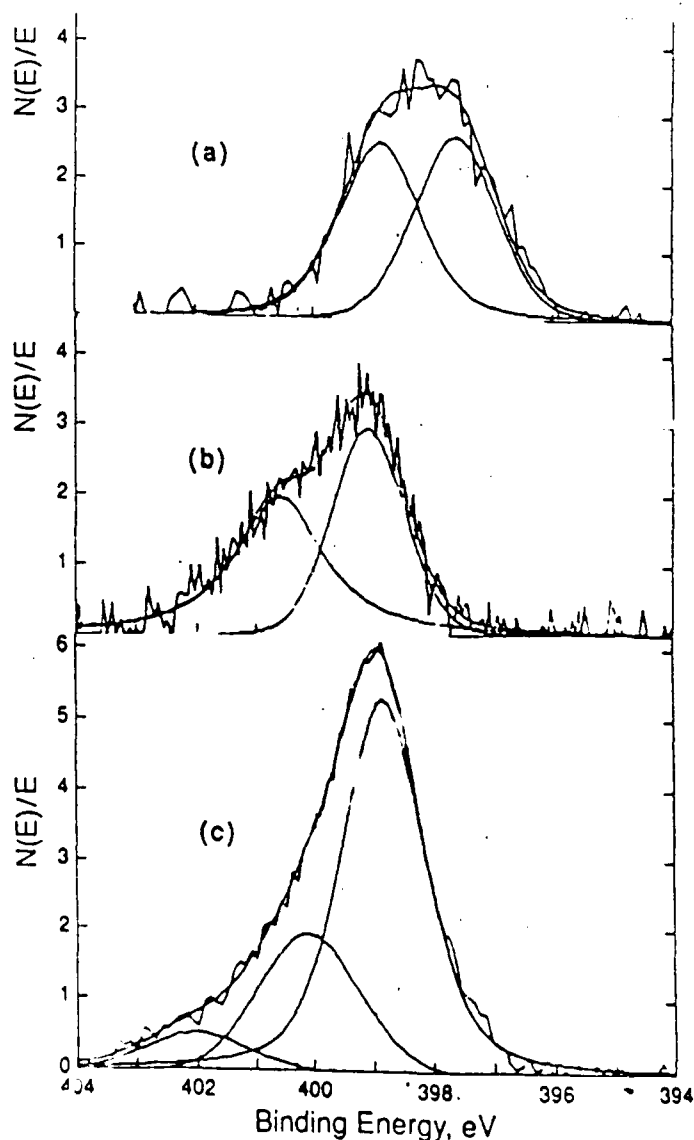


Fig. 2 N 1s XPS core level spectra of (a) emeraldine base, (b) sulfonated polyaniline and (c) emeraldine hydrochloride. The solid lines are the fit to the data.